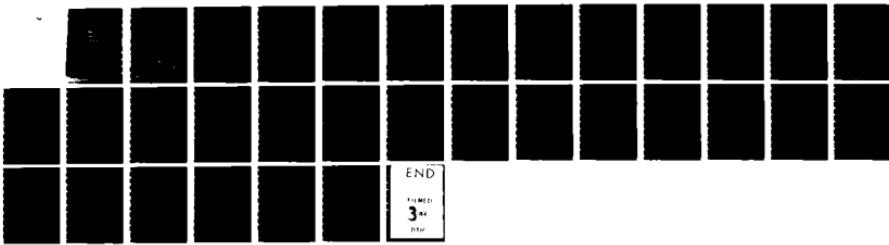


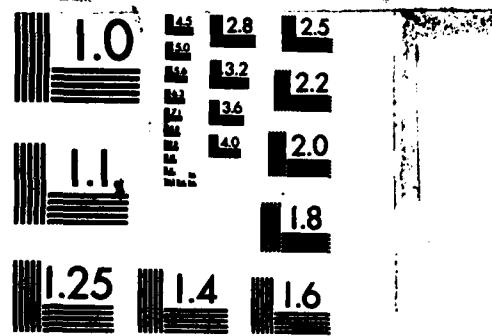
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Dry Chemical Development — A Model for the Extinction of Hydrocarbon Flames

C. T. EWING,* J. T. HUGHES,* AND H. W. CARHART

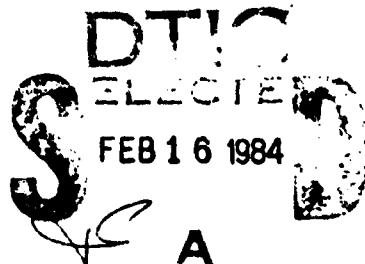
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An empirical relation has been developed which correlates and predicts the suppression effectiveness of a wide variety of gaseous, liquid, and solid agents. The flame extinguishment model is based on the premise that extinction is dominated by heat absorption processes and that a flame is extinguished when		

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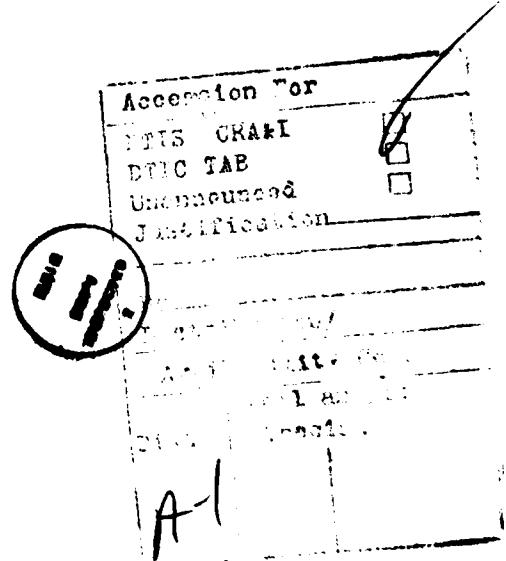
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sufficient heat has been removed by the extinguishant to reduce the temperature to a limit value. This limit is the minimum temperature at which the effective rate of the combustion reactions is sufficient to maintain flame propagation, and it depends in a predictable way on the properties of the suppressant and flame system. The heat-balance equation describing this is derived in two stages. In the first, a preliminary equation is obtained by considering only those substances which are thermally stable and act only as heat-capacity sinks. In the second, the equation is generalized by consideration of all endothermic reaction sinks, e.g., vaporization, dissociation, and decomposition. The general equation correlates most of the extinction data found in the literature. The results suggest that for many substances the extinguishing capacity is related to heat extraction and that many of the effects previously attributed to chemical mechanisms are thermodynamic in nature rather than kinetic.



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DRY CHEMICAL DEVELOPMENT - A MODEL FOR THE
EXTINCTION OF HYDROCARBON FLAMES

I. BACKGROUND

Various fire-extinguishing agents are carried on board Navy ships to control Class A (solid fuel), Class B (liquid and gas fuel), and Class C (electrical) fires. The resulting penalties in space, weight, and maintenance could be minimized significantly if a very effective multi-purpose agent suitable for Class A-B-C fires can be developed. Perhaps an even more important reason for this approach is that under duress of a fire situation the tendency is to "grab" the first fire extinguisher available and use it whether it is the best for that particular type of fire or not. Although there is some, but highly unquantified, effort to place a given type of fire extinguisher close to an area where the possibility of a particular type of fire might be higher, it has been noted on ship visits that there is no apparent consistency in placement and that extinguishers get moved as spaces are rearranged, especially on submarines. Therefore, an added argument is made for having a single dry-chemical extinguishing agent that would be highly effective for the more common types of Navy fires. It is the ultimate purpose of this R&D Project to develop a new-generations multipurpose dry-chemical agent that would be effective for Class A, B, and C fires. In the shorter range it was deemed desirable to examine how various agents work and to develop a predictive model for the extinguishment of hydrocarbon fires that could then be used in the design and development of the new agent. This would obviate the commonly used semi-random and

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more time consuming approach in the selection and mixing of various potential chemicals to yield the final multi-purpose agent. This report describes the development of such a model.

Literature related to fire fighting shows that there are a hundred or more potentially effective suppressants with widely differing chemical and physical properties. Chemical mechanisms have been proposed for different families of compounds; but these often do not provide quantitative information, and no framework could be found upon which to build a general relationship. The only requirement found to be common to the so-called "chemical suppressants" was that they must decompose and/or vaporize in the flame. This apparently general criterion suggested that mathematical expressions incorporating all energy sinks -- heat capacity, vaporization, and endothermic decompositions -- might be useful in explaining and correlating observed suppression. From a detailed study of possible physical mechanisms for flame extinguishment, it became apparent that an empirical relationship could be derived from a simple model for extinguishment based on the heat absorption processes which suppressants undergo in flames. The model is presented to stimulate thought and discussion in an area which has been largely overlooked in comparison to the extensive attention given to chemical mechanisms. Therefore, we first present the model, develop a general equation from it, and then illustrate its effectiveness in correlating and predicting the action on hydrocarbon-air flames of a wide variety of gases, liquids, and solid substances.

II. DEVELOPMENT OF MODEL

The model is derived for the action of chemicals on stoichiometric adiabatic hydrocarbon-air flames at atmospheric pressure. The development of the model, with the equations and assumptions related to it, is divided into two sections. In the first, preliminary relationships are derived for thermally stable substances which act only as heat-capacity sinks. In the second, endothermic reaction sinks are added and the preliminary relationships are expanded to incorporate other substances including volatile and dry-chemical suppressants.

Equation for Thermally Stable Gases

It has been shown by Tatem, et al., [1], Larson [2], and Sheinson, et al., [3], that dilution and heat-capacity factors satisfactorily explain the flame suppression by thermally stable, volatile agents. Diatomic gases such as nitrogen have high molar heat capacities and have been shown to be very effective in quenching flames [1]. Larson [2] used an index based on heat capacity to correlate the extinguishing effectiveness of many substances and argued on the basis of the degree of correlation that the primary mode of all inhibition is physical and that any inhibitor's effectiveness is adequately described by a thermal dilution mechanism. However, it has been shown by Sheinson, et al., [3], and by the work in this report that the heat-capacity sink alone does not adequately explain the unusual effectiveness of a so-called "chemical suppressant". Sheinson,

et al., (3), correlated physical suppression of the heat-capacity type and ascribed the excess effectiveness observed for several agents which dissociate as being due to a chemical mechanism. This report will later show that this effectiveness correlates with the contribution by endothermic decomposition sinks.

The adiabatic temperature, T_M , of a flame is commonly determined from an energy balance equating the heat liberated by the combustion reaction (at the initial temperature, T_0 , of the reactants which is normally 298°K) to the enthalpy gain of the products as they are heated from T_0 to T_M . This is the form which will be used here. However, for the development of the model the energy balance is based on the alternate thermodynamic path where the heat of combustion at the temperature of the flame is equated to the enthalpy gain of the reactants. This second form, which gives a more realistic picture of the actual processes which occur in flames, is

$$M_F Q_{T_M} = \int_{T_0}^{T_M} [Cp_{O2} + M_F Cp_F + \sum (M_I Cp_I)] dT + \sum (\alpha_M \Delta H_{T_M})_k + q \quad (1) +$$

where the symbol k represents consecutively the three dissociations: $CO_2 \rightleftharpoons CO + 1/2 O_2$, $H_2O \rightleftharpoons OH + 1/2 H_2$, and $H_2O \rightleftharpoons H_2 + 1/2$

+ See nomenclature for definition of terms

O_2 . This equates the heat generated chemically to the heat absorbed by all heat-capacity sinks and by the dissociations of carbon dioxide and water. The combustion energy in excess of that required by the heat sinks, q , is small and represents less than 3 percent of the total. It incorporates any errors in the thermal quantitites and in the simplifying neglect of the N_2 , O_2 , and H_2 dissociations.

When the equation above is restricted to saturated hydrocarbon air flames, it becomes

$$M_F Q_{T_{MA}} = \int_{T_0}^{T_{MA}} [Cp_{O_2} + M_F Cp_F + M_{N2} Cp_{N2}] dT + \sum (\alpha_M \Delta H_{T_{MA}})_k + q \quad (2) ++$$

Gudkovich, et al., (4) directly observed flame temperatures at and approaching extinction for both rich and lean hydrocarbon mixtures. Under normal conditions, no inconsistencies or discontinuities in temperature were observed. Their measured temperatures for lean flames were, within experimental error, equal to corresponding adiabatic values as computed thermodynamically, while those measured for rich flames were uniformly lower than adiabatic values. This was attributed to thermal losses possibly by radiation from soot in the flame. In any event, these facts suggest that nothing precipitous occurs in the hydrocarbon combustion process other than extinction at the limit. If one assumes, then, that combustion is normal and that the excess energy, q , is negligible at the limit, the conditions existing at the time of flame extinction can be represented by a simple heat balance,

$$M_{EI} \int_{T_0}^{T_{LI}} (Cp_{EI}) dT = M_F Q_{T_{LI}} - \int_{T_0}^{T_{LI}} [Cp_{O2} + M_F Cp_F + M_{N2} Cp_{N2}] dT - \sum (\alpha \Delta H_{T_{LI}}) k^{(3)} ++$$

This equation states that extinction occurs when the concentration of suppressant and the resulting heat extraction are sufficient to lower the temperature of the flame to its extinction limit T_{LI} . The application of the equation is based the premise that there is a unique temperature at extinction for each suppressant and that this temperature limit is determined by the minimum reaction rate required to sustain propagation and by the properties of the suppressant and flame system. It is also assumed that the extinguishant is added in a single step to a clean hydrocarbon-air flame and that all computations are independent of flame size and fuel consumption rates. To this end, all quantities are normalized per mole of oxygen or air.

The basic equation for thermally stable gases, when based on one mole of air rather than oxygen, is

++ Air is treated here as a mixture of N_2 and O_2 only; however, the value used for M_{N2} is normalized to 3.7584 moles N_2 /mole O_2 , so that $M_{N2} Cp_{N2}$ includes the heat capacity contribution by argon and other component gases in air.

$$M'_{EI} \int_{T_0}^{T_{LI}} (Cp_{EI}) dT = M'_F Q_{T_{LI}} - \int_{T_0}^{T_{LI}} (Cp_A + M'_F Cp_F) dT - \Sigma (\alpha M' \Delta H_{T_{LI}}) k^{(4)} + + +$$

and the equivalent equation based on the alternate path is

$$M'_{EI} \int_{T_0}^{T_{LI}} (Cp_{EI}) dT = M'_F Q_{T_0} - \int_{T_0}^{T_{LI}} [\Sigma (M'_i Cp_i) + M'_{N2} Cp_{N2}] dT - \Sigma (\alpha M' \Delta H_{T_0}) K^{(5)} + + +$$

where the symbol i refers consecutively to all major products of combustion -- H_2O , CO_2 , CO , O_2 , H_2 , and .

It is well known that adiabatic temperatures at different flammability limits and for different i + gas diluted hydrocarbon flames are not the same, but exhibit significant variation with the fuel, the suppressant, and the type of flame.

This has been demonstrated experimentally in the work by Gudkovich, et al., [4]. To illustrate the variability, temperature limits for a number of thermally stable gases are shown in Figure 1. These temperatures were computed for both diffusion and premixed flames by the program developed at NASA [5] and are for the extinction limits generated when the gaseous suppressants are added at concentrations sufficient to extinguish hydrocarbon-air flames. The required extinction concentrations were obtained from existing studies (3,6,7,8). For each type of flame the limit varies characteristically with the molecular weight of the suppressant molecules. The top curve

*** Air is treated here as a mixture of N_2 and O_2 only; however the value used for M'_{N2} is normalized to 3.7584 moles N_2 per mole of O_2 , so that $M'_{N2} Cp_{N2}$ and Cp_A include the heat-capacity contribution by argon and other component gases in air.

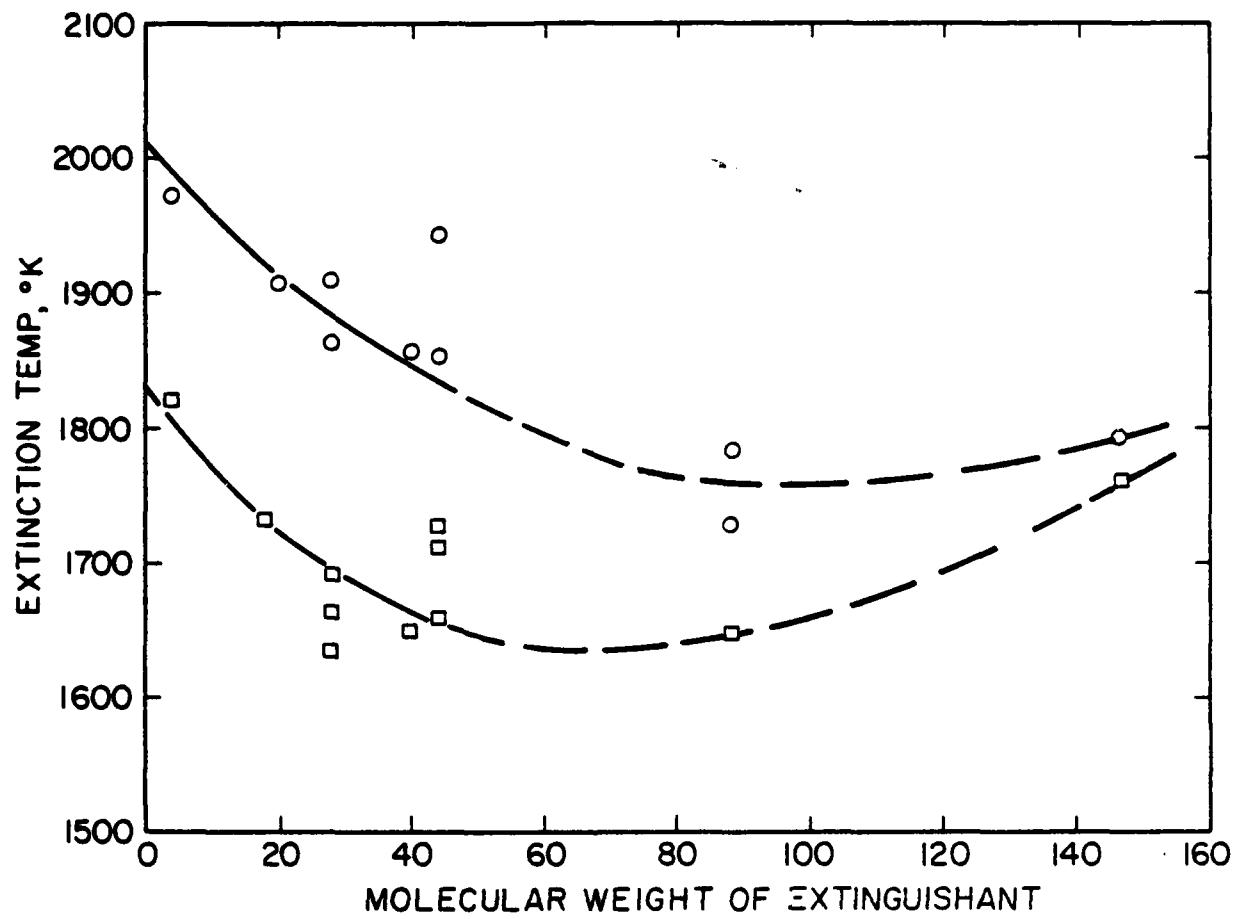


Figure 1

Calculated Extinction Temperature versus Molecular Weight for Several Thermally Stable, Gaseous Extinguishants; \circ , Diffusion and \square , Premixed Flames

represents T_{LI} values for diffusion flames and the lower curve gives corresponding values for premixed flames.

As a preliminary test of Equation 5, temperature limits were calculated for a number of thermally stable gases and compared in Table 1 to corresponding values computed with the NASA program (5). Heats of combustion for the calculations were obtained from Kanuary (9); heat-content and equilibrium data from JANAF (10). The limits derived from Equation 5 are only 0.8% higher for the diffusion flame and 1.7% higher for the premixed. Disagreements of this size can readily be explained by our neglect of the dimer dissociations and by minor differences in the thermal quantities used.

TABLE 1

COMPARISON OF THE TEMPERATURE LIMITS COMPUTED FROM EQUATION 5 WITH THOSE FROM THE NASA PROGRAM

Substance	Extinction Concentration (Mole % in Air)	T_{LI} Equation 5 (°K)	T_{LI} NASA Program (°K)
Diffusion Flame*			
A	40.5	1870	1856
Ne	36.9	1921	1907
He	31.8	1988	1972
N ₂	29.8	1877	1863
CO ₂	20.8	1875	1854
CF ₄	17.4	1736	1730
Premixed Flame**			
A	50.6	1676	1650
He	39.7	1848	1821
N ₂	38.9	1693	1665
CO ₂	24.9	1758	1729

Footnotes:

* For Heptane-air Diffusion Flames (3)

** For Methane-air Premixed Flames (7)

General Equation For All Substances

It has been assumed that Equations 4 and 5 represent, for a one-step addition of a pure heat-capacity extinguishant, the conditions existing in a hydrocarbon-air flame at the point of extinction. The equations may be modified to cover suppressants with endothermic reaction sinks if one accepts the following:

- 1) That an uninhibited flame is extinguished when the energy sinks (regardless of their type or combination) remove a quantity of heat sufficient to reduce the temperature to a characteristic limit,
- 2) That this limit temperature for any type of suppressant is set independently of the heat-balance equation by the minimum reaction rate required to sustain propagation and by the properties of the suppressant and flame system,
- 3) That the relative effectiveness of a suppressant is mathematically related to the level of the limit temperature -- the higher the limit temperature, the more effective the suppressant,
- 4) That many suppressants with heats of dissociation below 100^{-1} kcal/mole have a residence time and a reaction rate in the flame front which permit complete dissociation of the agent; and

- 5) That thermal dissociations of nitrogen, excess oxygen, and hydrogen are insignificant at all temperatures below 2300°K.

Assuming the above, the general relationship which represents the conditions existing in a hydrocarbon-air flame at extinction and which incorporates all known energy sinks is

$$M'_{EI} \left[\sum (R \Delta H)_{T_{LI}} \right] + \int_{T_0}^{T_{LI}} (C_p) dT]_{EI} = M'_F Q_{T_{LI}} - \int_{T_0}^{T_{LI}} [C_{pA} + M'_F C_{pF}] dT - \sum (\alpha M' \Delta H)_{T_{LI}} k \quad (6) + + +$$

and the equivalent equation based on the alternate path is

$$M'_{EI} \left[\sum (R \Delta H)_{T_{LI}} \right] + \int_{T_0}^{T_{LI}} (C_p) dT]_{EI} = M'_F Q_{T_0} - \int_{T_0}^{T_{LI}} [\sum (M'_i C_{p_i}) + M'_N C_{p_N}] dT - \sum (\alpha M' \Delta H)_{T_0} k \quad (7) + + +$$

The concentration (M'_{EI}) for a reactive suppressant represents a minimum value where particulate size permits all of the substance to react in the flame. With many dry-type agents, the original material decomposes early in the flame to generate secondary chemicals which also have endothermic reaction potentials. The equations, therefore, include a ratio, R, which represents the number of moles of each second chemical produced by one mole of the original agent. For example, each mole of sodium bicarbonate decomposes into 1/2 mole of sodium carbonate and the carbonate into the oxide and CO₂. Therefore, the effective enthalpy term $\sum (R \Delta H)$ becomes $(1 \times \Delta H_{NaHCO_3} + 1/2 \times \Delta H_{Na_2CO_3})$.

III. A POSSIBLE EXPLANATION FOR VARIATION OF THE TEMPERATURE AT THE EXTINCTION LIMIT

We have seen in the section dealing with the thermally stable gases that the temperature at the extinction limit (T_{LI}) depends on the properties of the diluent and flame system (Figure 1). Corresponding temperature limits for substances which are more effective in extinguishing flames (including the particulate solids and liquids, and gaseous Halons) also appear to depend on the properties of the extinguishant and flame system. The variation of this limit becomes more plausible if one assumes that ignition for hydrocarbon flames is readily sustained and that the extinction limit is the minimum flame temperature at which the effective rate of the combustion reactions is sufficient to maintain the flame velocity required for propagation. This rate depends on a complex balance between the generation of free atoms and radicals through bimolecular reactions and their removal through ter-molecular reactions (11,12). The two types have different temperature dependencies. Bi-molecular reactions vary exponentially while ter-moleculars vary inversely with temperature. In addition, the recombination reaction rates would be expected to depend on pressure, on dilution effects, and on the properties of third-body diluent molecules. These factors could account for variation of the limit.

IV. APPLICATION OF MODEL

The temperature of a flame when enough of an inert gas is added to bring about extinguishment has been shown to depend on the properties of the suppressant, and the level of T_{LI} for any thermally stable gas may be approximately predicted from its molecular weight and Figure 1. For the "chemical suppressant", on the other hand, there is no molecular weight or comparable measure which can be used to predict the value of T_{LI} . Fortunately, any "chemical" inhibitor may be classified in one of three large groups where all substances within a group appear to have common extinguishing properties and, more importantly, a common value for the limit temperature. For example, all suppressants which are used in the liquid or solid state can be classified under one group. These condensed substances, when in the proper state of dispersion, have maximum known effectiveness in extinguishing flames, and a common value of 2165°K for T_{LI} is satisfactory for all saturated hydrocarbon flames. This rather high value of T_{LI} for each condensed suppressant (and the correspondingly small difference between the adiabatic temperature of the clean air flames (9) and that at extinction) is consistent with existing literature (13-17).

Commercial solid extinguishants vary widely in their properties and in their shape and form. Physical factors determine the effectiveness of a particular type of heat sink. Therefore, they must be considered and guidelines must be set so that

Equation 7 can be applied correctly and so that experimental values may be selected correctly for comparison purposes.

A distinction must be made between decrepitating and non-decrepitating solids. A decrepitating material is one which decomposes in the flame producing particles of sub-micron size; a non-decrepitating material is one which evaporates or decomposes without breakup. For those non-decrepitating solids, which decompose and/or vaporize to produce saturation or gaseous decomposition pressures greater than 10^{-6} atmospheres, it has been demonstrated (18-20) that particles below 5-10 microns are completely vaporized or decomposed in the reaction zone of hydrocarbon-air flames. For example, Iya, et al., (20) proved experimentally with a premixed air flame that sodium bicarbonate of 0-10 micron particle size is completely vaporized before leaving the reaction zone. They used absorption spectroscopy to show that the sodium concentration in the flame did not increase with distance above the burner.

It has, in contrast, been demonstrated experimentally (18, 19, 21) that the effectiveness of a solid, non-decrepitating substance at particle sizes above 5 to 10 microns is often proportional to the surface area (per unit volume of gases) of the solid presented to the flame. This is consistent with the model presented, since the effectiveness of a substance in extinguishing flames could be severely limited by the rate at which it can decompose and/or volatilize from the solid surface presented to the flame. In fact, this is often the rate-limiting step for any physical mechanism involving an endothermic heat of

reaction. Therefore, extinction concentrations observed for solids at larger particle sizes are not minimum values and are not suitable for comparison with values predicted from Equation 7.

The characteristics of decrepitating solids are completely different from those just described for non-decrepitating types. For a given set of flame conditions and for any substance which decomposes or decrepitates at a lower temperature to a second solid of high surface area, there is usually an optimum size of the original particle below which decomposition occurs before the flame reaction zone is reached, and above which decomposition is limited by the residence time of the particles in the flame (19, 22). How closely the optimum, or maximum, effectiveness of a decrepitating substance matches that which would be predicted from Equation 7 is not known.

There is a large group of highly volatile or gaseous substances, including bromine- and iodine-containing compounds, which can be assumed to be completely dissociated in or near the reaction zone of the flame. They have inhibiting effectiveness lower than that for the liquids and solids. Their effectiveness, as with thermally stable gases, differs significantly for the two flame types. There appears to be a common T_{LI} of 2015°K for diffusion and 1900°K for premixed hydrocarbon flames. From an inspection of Figure 1, it can be seen that the 115° difference between the limit temperatures for the two flame types is roughly consistent with that observed for thermally stable gases at lower molecular weights.

There is a second group of very volatile liquid or gaseous substances, including chlorine and many organics containing chlorine which would be expected to have degrees of dissociation significantly below unity at the temperatures they might be expected to reach in the air flame. For example, chlorine at 1500°K is only 5 to 10% dissociated (23). In order to allow the use of a numerical treatment for incomplete dissociation, we will assume that all substances in this group achieve a dissociation of 30% and that they have the same common temperature limits as the other group--2015°K for diffusion and 1900°K for premixed flames. It should be recognized that many compounds in this group decompose in steps, and that the effective change in enthalpy for the overall reaction (based on a 30% dissociation for each step) will be only a fraction of the enthalpy change for a single step.

The guidelines that have been presented above for applying Equation 7 to predict the minimum concentrations at extinction for a wide variety of chemical substances can be summarized (Table 2). The letters A,B,C and D have been assigned to the four groups and will be used throughout the remainder of the report to identify the group to which each substance is assigned and the properties which influence the various heat sinks.

TABLE 2
GROUPING OF SUBSTANCES FOR PREDICTING WITH EQUATION 7
THE MINIMUM CONCENTRATION REQUIRED TO EXTINGUISH
HYDROCARBON-AIR FLAMES

GROUP	DESCRIPTION OF SUBSTANCES	T_{LI} VALUES
<u>Solids and Liquids</u>		
A	non-decrepitating solids (particle size 5-10 microns)	2165°K*
and		
	liquids or metal compounds dissolved in liquids	
<u>Gases</u>		
B	gases and volatile liquids which can be assumed to be completely dissociated in the flames	2015°K* (diffusion flames) 1900°K* (premixed flames)
C	gases and volatile liquids which have a dissociation in the flame of less than unity	2015°K (diffusion flames) 1900°K (premixed flames) (NOTE: effective ΔH for chlorine containing compounds based on thermal dissociation level for each step of 30%)
D	gases which are thermally stable in the flame	T_{LI} (Figure 1)

*Value required to correlate literature results

Minimum concentrations required to extinguish hydrocarbon-air flames have been calculated from Equation 7 for a number of gases, liquids, and solids. These are presented in Table 3 and

compared to corresponding experimental values. Except for chlorine and organics containing chlorine, the calculated and experimental concentrations for each substance in the table represent optimum, or maximum, flame extinguishing effectiveness. For example, each particulate solid or liquid is assumed to be completely decomposed and/or vaporized in the flame and each gaseous substance to be completely dissociated. All experimental figures were derived from studies on common hydrocarbon-air flames (one atmosphere) of the adiabatic type with fuel-to-oxygen ratios approaching stoichiometry. Each value predicted from Equation 7 is calculated for the fuel and flame type used in generating the corresponding experimental value. When the substance is a gas or a highly volatile liquid (groups B, C, and D), concentrations required to extinguish diffusion and premixed flames will differ, so each line of data represents a single fuel and a single flame type. The fuel is identified along with the name of the substance and the flame type with the designator P (premixed) or D (diffusion) following the reference.

For each substance included in the table, quantities used for evaluating reaction and heat-capacity sinks are included. It should be recognized that there are two thermodynamic paths between the initial state which is the unreacted extinguishant at T_0 and the final state which consists of the products of the endothermic reactions at the maximum temperature of the flame, T_{LI} . On one path -- the only one considered to this point in the article -- the unreacted extinguishant is heated from T_0 to T_{LI} and the reactions take place at T_{LI} . On the second path,

the endothermic reactions are hypothetically carried to completion at T_0 and the products then heated from T_0 to T_{LI} . According to Hess' law (9) both these paths have the same total heat change. The heat-absorption quantities presented in the table are generally based on the second path, and the heat sinks were evaluated as follows:

$$[\sum(R\Delta H_{T_{LI}}) + \int_{T_0}^{T_{LI}} Cp dT]_{EI} = [\sum(R\Delta H_{T_0}) + \sum \int_{T_0}^{T_{LI}} (R_j Cp_j) dT]_{EI} \quad (8)$$

where j represents the products of extinguishant decomposition and/or vaporization. The required thermodynamic quantities were obtained from JANAF (10) and from (24-27). It was necessary to estimate reaction enthalpies for some larger molecules by bond additivity rules [28] and these are identified by enclosing them in parentheses. The reaction enthalpy value listed for each substance represents a summation of all its effective endothermic reactions, and those for the chlorine-containing compounds reflect the 30% dissociation on each step.

TABLE 3
COMPARISON OF PREDICTED EXTINGUISHING
CONCENTRATIONS (EQUATION 7) WITH EXPERIMENTAL
VALUES

Chemical Substances	$\sum \int_{T_0}^{T_{LI}} (R_j C_p j) dt \sum (R \Delta H_{T_0})$		Predicted	Experimental	References
	kcal. mole	kcal. mole	Mole % in Air Diff. Premix	Mole % in Air	
GROUP A -- SOLIDS AND LIQUIDS ($T_{LI} = 2165^{\circ}\text{K}$)					
Na ₂ CO ₃ (CH ₄)	70.9	87.1	.65	.53	18P ¹
NaHCO ₃ (CH ₄)	57.3	59.7	.88	1.9, 1.7, 1.3, .33	21P, 20P, 18P ¹ , 13
KHCO ₃ (CH ₄)	47.2	128.6 ³	.59	.57	18P ¹
AlCl ₃ (CH ₄)	36.3	29.0	1.6	1.2	21P
NaCl (CH ₄)	16.95	54.9	1.4	1.0	18P ¹
H ₂ O (Mist) (nC ₈ H ₁₈)	19.41	10.52	5.2	5.0 ± 1	31D
Br ₂ (nC ₈ H ₁₈)	19.42	53.5	2.2	2.3	29P
I ₂ (nC ₈ H ₁₈)	18.69	51.1	2.3	(Generally 2.3 equal Br ₂)	29P
Fe(CO) ₅ (C ₂ H ₅ OH)	93.2	54.1	1.2	1.7	30D ²
Na(C ₂ H ₅ O ₂) (C ₂ H ₅ OH)	107.9	(238)	.50	.57 - .69	30D ²
Pb(CH ₃ CO ₂) ₂ (C ₂ H ₅ OH)	216.0	(270)	.36	.29	30D ²
NaOH (C ₂ H ₅ OH)	22.07	51.5	2.4	2.3	30D ²
GROUP B -- GASES ($T_{LI} = 2015^{\circ}\text{K}$ Diffusion and 1900°K Premixed)					
CF ₃ Br (nC ₈ H ₁₈)	39.5	69.4	3.2	3.1, 3.5, 3.8, 3.3	32D, 33D, 34D
CF ₃ Br (nC ₈ H ₁₈)	39.5	69.4	3.2	3.3	32D
CF ₃ Br (nC ₈ H ₁₈)	36.6	69.4	4.5	4.9	37P
CF ₃ Br (nC ₈ H ₁₈)	39.5	69.4	3.3	3.7, 2.8	32D, 35D
CF ₃ Br (nC ₈ H ₁₈)	(Fuel at 150°C)	4.0		4.0	32D
CF ₃ Br (C ₂ H ₅)	39.5	69.4	3.3	3.9, 2.9	32D, 33D
CF ₃ Br (CH ₄)	39.5	69.4	2.7	2.5, 1.3	32D, 33D
CF ₃ Br (CH ₄)	36.6	69.4	4.1	4.7	36P ⁴
CF ₃ Br (C ₂ H ₅ OH)	39.5	69.4	3.3	3.9	32D
C ₂ F ₅ Br ₂ (nC ₈ H ₁₈)	66.3	82.6	2.4	2.1	32D
C ₂ F ₅ Br ₂ (nC ₈ H ₁₈)	61.5	82.6	3.4	3.2-3.3	37P
C ₂ F ₅ Br (nC ₈ H ₁₈)	66.3	82.6	2.4	2.1	32D
C ₂ F ₅ Br ₂ (C ₂ H ₅ OH)	66.3	82.6	2.4	2.4	32D
CF ₃ Br ₂ (nC ₈ H ₁₈)	39.6	102.4	2.5	2.4	32D
CF ₃ Br ₂ (CH ₄)	36.8	102.4	3.1	3.8	36P ⁴
CH ₃ Br (C ₂ H ₅)	33.6	70.6	3.4	3.1	35D
CH ₃ Br (CH ₄)	31.0	70.6	4.2	4.7	5P
CH ₃ Br (nC ₈ H ₁₈)	33.6	70.6	3.4	5.1	32D
CH ₃ I (CH ₄)	30.7	57.1		4.8 (same as CH ₃ Br(CH ₄) above 14)	
GROUP C -- GASES ($T_{LI} = 2015^{\circ}\text{K}$ Diffusion and 1900°K Premixed)					
Cl ₂ (nC ₈ H ₁₈)	15.1	17.4	13.4	10.9	29P
CF ₃ Cl (nC ₈ H ₁₈)	40.3	25.7	5.2	7.8	32D
CFCI ₃ (nC ₈ H ₁₈)	41.4	30.1	4.9	7.0	32D
CHCl ₃ (nC ₈ H ₁₈)	38.4	35.2	6.4	6.1	29P
CCl ₄ (nC ₈ H ₁₈)	39.4	32.3	6.6	4.6	29P
HCl (nC ₈ H ₁₈)	14.5	30.9	7.5	7.6	38D

Chemical Substances	$\sum_{T_0}^{T_{LI}} (R_j C_p_j) dT \sum (R \Delta H_{T_0})$		Predicted Mole % in Air Diff. Premix	Experimental Mole % in Air	References
	kcal. mole	kcal. mole			
GROUP D -- THERMALLY STABLE GASES (T _{LI} from Figure 1)					
CF ₂ (nC ₂ H ₁₀)	33.1	16.6	17.4	21.0	3D 8P
CF ₃ (nC ₂ H ₁₀)	30.3	20.5			
CO ₂ (nC ₂ H ₁₀)	13.5	22.7	20.8	31.8	3D 37D
CO ₂ (nC ₂ H ₁₀)	16.9	31.4			
He (nC ₂ H ₁₀)	8.41	32.0	31.8	39.2	3D 39D
He (CH ₄)	7.49	42.6			
H ₂ O ₂ (CH ₄)	14.16	31.1	29.6	39.6	39P

- 1) Value is from velocity versus suppressant concentration diagram but is based on concentration of suppressant at extinction rather than an extrapolation of the initial slope.
- 2) Vanpee, et al., reports Mole Merit Number as observed at extinction; corresponding mole fraction of inhibitor at extinction taken to be the reciprocal of this number.
- 3) The reaction enthalpy of KHCO₃ is higher than that of NaHCO₃ since the oxide of potassium would be expected to decompose in the flame.
- 4) Temperature of mixture is at 75°C, so T₀ in Equation 7 is 345°K.

For two common halogenated extinguishing agents - CF₃Br (Halon 1301) and C₂F₃Br₂ (Halon 2402) - computed and experimental extinction concentrations are compared in Table 3 for several different fuels. The relative effectiveness figures shown for these two substances are typical of those found for other Halons. As a general rule, any air flame of a saturated normal hydrocarbon fuel, except methane, requires the same concentration (within 5 to 10%) of a suppressant for extinguishment. The nonconforming properties of the methane flame are well known, and Equation 7 predicts that this flame should

require, for a given inhibitor, an extinguishing concentration which is 30 to 40% lower than that required by flames of the higher, saturated hydrocarbons.

Equation 6 or 7 can be used to predict the concentration of a suppressant which is required to extinguish a flame where the suppressant and/or reactants are at temperatures above ambient. For this type of calculation, either equation is solved using properly adjusted values for the heat sinks and for the initial temperatures of the suppressant and the reactants. This is illustrated in the table for CF_3Br and the butane flame. The equation predicts the minimum concentrations required experimentally to extinguish two butane flames -- one where the entering fuel is at ambient temperature and the other where it is preheated to 150°C .

For the solids and liquids (Group A) included in Table 3, the majority of the fuels used experimentally for obtaining the comparison literature values are saturated hydrocarbons. The only exception is ethanol which was used by Vanpee, et al. [30]. It was noted in [32] that the concentration of a substance required to extinguish the ethanol flame is approximately equal to that required for flames of the higher saturated hydrocarbons. So, for four of the substances included in Group A we have compared concentrations predicted for the $n\text{C}_4\text{H}_{10}$ flame with those observed for the ethanol flame. The validity of this procedure is illustrated in the table for CF_3Br and $\text{C}_2\text{F}_4\text{Br}_2$.

V. DISCUSSION

Experimental extinction concentrations have been derived from flame velocity studies (18,29) at low suppressant concentrations by extrapolating the initial changes in velocity. Extinction concentrations obtained by this procedure for "chemical" suppressants are significantly smaller than corresponding values predicted with Equation 7. However, it is well known (18,29,40,41) that the change in burning velocity is not linear with suppressant concentration and that this non-linearity is most pronounced at lower concentrations. Therefore, the initial slope predicts an erroneously low extinction concentration and experimental results derived in this way are not included in Table 3.

The extinguishing concentration as calculated for H_2O (mist) represents a finely divided state which can be vaporized in the flame front. The corresponding experimental value (31) represents the minimum concentration of mist required to extinguish a diffusion type hexane pan fire in an enclosed chamber. This is an engineering value with an accuracy of about $\pm 20\%$, which is better than that often associated with experimental work on dry chemicals. In any event, the experimental value agrees in magnitude with that predicted from the model. In the case of water, this is of unique significance since it is accepted throughout the literature that vaporization of water [41-44] is involved in the cooling and extinction of flames. It is

interesting that the heat-absorption sink for vaporization of H_2O is universally accepted while vaporization and dissociation sinks for other substances are ignored.

Our continuing survey of the literature shows that a large number of different methods have been used for inhibition and extinction studies. The lack of standardization in both the experimental methods and in the measures used for reporting effectiveness of extinguishants makes comparison difficult. As a consequence, results often cannot be interpreted, and those which can be are scattered and often poorly characterized. Therefore, any model for flame extinguishment cannot be fully substantiated until additional and careful measurements have been made of the minimum concentrations of substances which are required to extinguish well-characterized flame systems.

The authors recognize that flame extinguishment might be explained by many factors, including heat-capacity sinks, reaction sinks, dilution effects, particle momentum, flame restriction effects, cooling effects of surfaces adjacent to flame, chemical inhibition, and heterogeneous or homogeneous chain termination mechanisms. It appears, however, that the high extinguishing effectiveness of many "chemical inhibitors" can be predicted physically from the relationship for heat-capacity suppressants by incorporating the additional heat-absorption sinks resulting from vaporization, decomposition, or dissociation of the inhibitor. The model effectively correlates and predicts minimum concentrations of substances which extinguish flames. This suggests that for substances other than H_2O

the heat-absorption processes which occur in flames are more important than previously recognized. Thus, decomposition, dissociation and vaporization may explain many of the effects otherwise believed to be "chemical".

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VII. NOMENCLATURE

C_p	Heat capacity, cal mole ⁻¹ K ⁻¹
M	Concentration of substance, moles/mole oxygen
M'	Concentration of substance, moles/mole air
Q	Heat of combustion, cal/mole fuel
q	Combustion energy in excess of that required for all major energy sinks, cal/mole oxygen
R	Moles of a second product produced per mole of the original substance
ΔH	Change in enthalpy of a reaction, cal/mole
T_M	Adiabatic temperature of hydrocarbon flame, °K
T_{MA}	Adiabatic temperature of hydrocarbon-air flame, °K
T_0	Initial temperature of reactants and suppressant, normally 298°K
T_{LI}	Adiabatic temperature of the flame at extinction, °K
α	Fractional degree of dissociation
E_I	Suppressant for which flame extinguishing concentration is added
N_2	Nitrogen already present in stoichiometric flame front before the addition of M_{E_I}
F	Fuel
I	Any suppressant present in flame front
O_2	Oxygen
CO_2	Carbon Dioxide
A	Air
i	Any one of several products from combustion of hydrocarbon - H_2O , CO_2 , CO , O_2 , H_2 , and OH
j	Any product from extinguishant decomposition and/or vaporization
k	Any one of three dissociations: $CO_2 \rightleftharpoons CO + 1/2O_2$, $H_2O \rightleftharpoons OH + 1/2H_2$, or $H_2O \rightleftharpoons H_2 + 1/2O_2$.

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